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(54) Title: STYRENE MONOMER POLYMERIZATION INHIBITION USING SUBSTITUTED DIHYDROXYARENES AND NITROXIDES (57) Abstract It has been discovered that the polymerization of vinyl aromatic compounds, such as styrene, may be inhibited by the addition of a composition that contains a dihydroxyarene or an alkyl-dihydroxyarene, a hydrogen transfer agent, and a stable nitroxide. In another, preferred embodiment of the invention, these three components are blended in an organic amine.		

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STYRENE MONOMER POLYMERIZATION INHIBITION USING SUBSTITUTED DIHYDROXYARENES AND NITROXIDES

Field of the Invention

5 The present invention relates to methods and compositions for inhibiting the polymerization of vinyl monomers, and more particularly relates, in one embodiment, to methods and compositions for inhibiting the polymerization of vinyl aromatic monomers.

Background of the Invention

10 It is well known that undesirable and costly polymerization is a significant problem during the manufacturing of various vinyl monomers, particularly vinyl aromatic compounds, such as styrene. Many kinds of inhibitors have been used in the past to minimize this problem. For instance, inhibitors such as diethylhydroxylamine, phenyl-*p*-phenylenediamines, *tert*-butyl catechol, and phenothiazine have been used to control
15 polymer formation. During the early 1980s, compounds selected from the groups called alkyl-substituted di-nitro-phenols and nitroso-phenols found widespread use in the styrene industry. However, because such compounds also functioned as insecticides or were dangerous to handle, their use has been discouraged by environmental and government agencies.

20 Recently, a new class of compounds called stable free radicals is being investigated to replace the nitrophenol products. Although stable free radicals are effective on monomer polymerization, their current cost makes them unattractive. It would be desirable if a composition and method could be devised to overcome some of the problems in using the stable free radical polymerization inhibitors.

25

Summary of the Invention

 Accordingly, it is an object of the present invention to provide a method and composition to effectively inhibit the polymerization of vinyl aromatic compounds, such as styrene.

30 It is another object of the present invention to provide a method and composition to effectively inhibit the polymerization of styrene that is less expensive than using stable free radicals exclusively.

 Still another object of the invention is to permit use of a composition to effectively inhibit the polymerization of styrene that has little or no environmental concerns.

35 In carrying out these and other objects of the invention, there is provided, in one form, a composition for inhibiting polymerization of vinyl aromatic compounds that includes a dihydroxyarene, a hydrogen transfer agent, and a stable nitroxide.

Detailed Description of the Invention

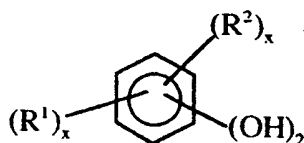
It has been discovered that the combination of a dihydroxyarene or a substituted alkyl-dihydroxyarene, a hydrogen transfer agent, and a stable nitroxide is an effective treatment to control styrene monomer polymerization. This treatment protocol is most effective when formulated in an organic amine, although the composition may find effective use without the organic amine.

It is expected that suitable vinyl aromatic monomers that may be polymerization inhibited by the compositions and methods of this invention include, but are not necessarily limited to styrene, substituted styrene, divinylbenzene, vinyltoluene, vinyl naphthalene, polyvinylbenzenes, and isomers thereof. Preferably, the aromatic monomer is styrene. It is anticipated that this invention could also inhibit the polymerization of non-aromatic vinyl compounds, *e.g.* acrylonitrile, vinyl chloride, acrylic acid and the like.

15 Dihydroxyarenes

Suitable substituted alkyl-dihydroxyarenes for the polymerization inhibiting composition of the invention may include, but are not necessarily limited to, substituted alkyl-dihydroxybenzenes having the formula:

20



where R^1 and R^2 are the same or different and are independently selected from the group consisting of hydrogen, straight, branched, and cyclic alkyl groups averaging from about 1 to about 6 carbon atoms, preferably from about 1 to about 4 carbon atoms, and where x averages from about 0 to about 9, and preferably in one embodiment from about 1 to about 9. In one preferred embodiment, both R^1 and R^2 are not simultaneously hydrogen.

Examples of specific substituted alkyl-dihydroxyarenes that would be suitable in the composition of this invention include, but are not necessarily limited to, hydroquinone; *tert*-butylhydroquinone; 2,5-di-*tert*-butylhydroquinone; *tert*-butylcatechol; hydroquinone; 3,5-di-*tert*-butylcatechol; catechol; 3,3,3',3'-tetramethyl-1,1'-spiro-bis-indane-5,5',6,6'-teterol; and mixtures thereof.

Hydrogen Transfer Agent

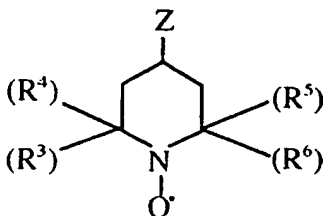
It is anticipated that any compound which readily donates hydrogen would be expected to be useful. Hydrogen transfer agents suitable for use in the polymerization inhibiting composition of this invention include, but are not necessarily limited to,

naphthalene; anthracene; decalin; hydroquinoline; 1,2,3,4-tetrahydronaphthalene (TETRALIN®; DuPont); 9,10-dihydroanthracene; fluorene; squalane; squalene; tetramethylhydroquinoline; and mixtures thereof.

5 Stable Nitroxide

The stable nitroxide of the composition useful for inhibiting polymerization of vinyl aromatic compounds may include, but are not necessarily limited to those having the formula:

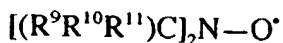
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15 where R^3 , R^4 , R^5 , and R^6 are the same or different and are independently selected from the group consisting of straight, branched, or cyclic alkyl groups of from 1 to about 9 carbon atoms, preferably from about 1 to 3 carbon atoms; where Z is selected from the group consisting of hydrogen, oxygen, alkyl groups, alkoxy groups, hydroxyl, aryl groups, alkaryl groups, heterocyclic alkyl groups; and where when Z contains carbon
20 atoms, may contain an average of from about 1 to 9 carbon atoms, preferably from about 1 to 3 carbon atoms. Within this definition, R^3 and R^4 may be joined together to form a cyclic moiety which may be alkylene or aralkylene. The same is true for the R^5 and R^6 pair.

25 Examples of specific stable nitroxides that would be suitable in the composition of this invention include, but are not necessarily limited to, 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO); 4-OXO TEMPO; 1-oxyl-2,2,6,6-tetramethylpiperidine; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one; 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl-2-acetate; 1-oxyl-2,2,6,6-tetramethyl-1-piperidin-4-yl-2-ethylhexanoate and mixtures thereof.

30 In an alternate definition, the stable nitroxides may include, but are not necessarily limited to those having the formula:



35 where R^9 , R^{10} , and R^{11} are independently selected from the group consisting of hydrogen, straight, branched or cyclic alkyl, aryl, aralkyl, and alkaryl moieties; where only one of R^9 , R^{10} , and R^{11} on each C can be hydrogen at a time; where one or more of R^9 , R^{10} , and R^{11} on one C may be joined to a R^9 , R^{10} , and R^{11} on the other C to form a cyclic moiety selected from the group consisting of alkylene, and aralkylene moieties;

where any two of the R^9 , R^{10} , and R^{11} on any one C may be joined together to form a cycloalkyl; where any of the above definitions of R^9 , R^{10} , and R^{11} may contain one or more heteroatoms selected from the group consisting of N, O and S; and where the total number of carbon atoms in the hindered secondary hydroxylamine ranges from 6 to 70.

5

Organic Amine

Organic amines suitable in the methods and compositions of this invention may include, but are not necessarily limited to, organic amines of the formula:



10 where R^7 and R^8 are the same or different and are independently selected from the group consisting of hydrogen; straight, branched, and cyclic alkyl groups; alkoxy groups; hydroxyalkyl groups; and aminoalkyl groups; averaging of from about 1 to about 20 carbon atoms, preferably from about 6 to about 9 carbon atoms, where both R^7 and R^8 are not simultaneously hydrogen.

15 Examples of specific organic amines that would be suitable in the composition of this invention include, but are not necessarily limited to, butylamine; hexylamine; n-octylamine; dodecylamine; cyclohexylamine; N,N-dihexylamine; ethanolamine; N-(2-aminoethyl)ethanol; ethylenediamine; 2-aminopropanol; and mixtures thereof.

20 Proportions

A number of factors affect the effective amounts of the alkyl-dihydroxyarenes, hydrogen transfer agents, and stable nitroxides of this invention that would be useful to inhibit the polymerization of a vinyl compound, including, but not necessarily limited to, the nature of the vinyl compound, the concentration of the vinyl compound, the
25 temperature and pressure environment of the vinyl compound, the nature of the particular alkyl-dihydroxyarenes, hydrogen transfer agents, and stable nitroxides used, and the like. Nevertheless, some general guidelines as to the effective proportion of the alkyl-dihydroxyarenes, hydrogen transfer agents, and stable nitroxides in the vinyl compound may be given.

30 If the organic amine is not present, the composition of this invention may have from about 1 to about 10,000 ppm of the alkyl-dihydroxyarene; from about 1 to about 10,000 ppm of the hydrogen transfer agent; and from about 1 to about 10,000 ppm of the stable nitroxide, based on the total amount of vinyl aromatic compound being treated. Preferably, the proportions range from about 34 to about 200 ppm of the alkyl-
35 dihydroxyarene; from about 34 to about 118 ppm of the hydrogen transfer agent; and from about 34 to about 145 ppm of the stable nitroxide, based on the total amount of vinyl aromatic compound being treated.

If the organic amine is present, then the composition of this invention may have from about 1 to about 10,000 ppm of the alkyl-dihydroxyarene; from about 1 to about 10,000 ppm of the hydrogen transfer agent; from 1 to about 10,000 ppm of the stable nitroxide and from about 1 to about 10,000 ppm of the organic amine, based on the total amount of vinyl aromatic compound being treated. Preferably, the proportions range from about 34 to about 200 ppm of the alkyl-dihydroxyarene; from about 34 to about 118 ppm of the hydrogen transfer agent; from about 34 to about 145 ppm of the stable nitroxide and from about 5 to about 300 ppm of the organic amine, based on the total amount of vinyl aromatic compound being treated.

The components of the composition may be simply mixed together. They may be mixed together in a single composition prior to addition to the vinyl aromatic compound, although they may also be added to the vinyl compound separately.

The invention will be further illustrated with respect to specific examples, which are not intended to limit the invention, but rather to more fully describe it.

Test Method

In order to evaluate the effectiveness of the invention, the following method was employed. It is best to prevent the presence of residual oxygen in the reaction vessels during testing. Oxygen has been shown in the literature and laboratory results to increase the activity of some inhibitors in preventing styrene polymerization.

Inhibited styrene monomer purchased from Aldrich Chemicals was distilled under vacuum (45°C, 29 mm Hg) to remove the conventional storage inhibitor 4-*tert*-butylpyrocatechol. The distilled styrene was checked for polymer content by sampling a portion and mixing in cold methanol. The distillation of the styrene monomer is considered successful if the two liquids mix completely with no presence of haze or cloudy appearance. One hundred mls of distilled styrene was transferred into a 250 ml, three-necked, round bottom reaction flask. The desired amount of inhibitor(s) were added to the distilled styrene monomer. The reaction flask was also equipped with a condenser, a thermocouple (type J), thermometer (Celsius), and a gas sparge tube.

The reaction apparatus was placed in an oil bath. The temperature of the oil bath could be raised by the use of an external heating device. The styrene monomer was purged with nitrogen for 20 minutes to insure that the effect of oxygen on styrene monomer and/or inhibitors would be insignificant during the test run. While continuing the nitrogen purge, the temperature of the oil bath and subsequently, the styrene/inhibitor(s) composition was raised until a styrene monomer/inhibitor(s) composition temperature of 118°C \pm 2°C was obtained. The styrene monomer/inhibitor(s) composition was maintained under these conditions for 90 minutes.

- The reaction flask apparatus was removed from the hot oil bath and the styrene monomer/inhibitor(s) composition was allowed to cool to ambient under continuing nitrogen purge. The styrene monomer/inhibitor(s) composition was transferred from the reaction flask into a 1000 ml beaker containing 200 ml of cold methanol. The
- 5 styrene/methanol mixture was mixed until the polymer, if any, agglomerates. Eight hundred ml of n-heptane was added to the styrene methanol composition. The polystyrene, if any, was allowed to settle out of solution until the liquid phase of the composition was clear. The styrene/methanol/n-heptane/polymer mixture was filtered through a 1.0 μ m glass fiber filter. Any remaining polymer was washed from the beaker
- 10 with n-heptane through the glass fiber filter paper. The filter paper was placed into an oven with ventilation capable of maintaining a temperature of $150^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 16 hours. The dried polymer was cooled in a desiccator, and the weight of the polymer was obtained by taking the difference of the weight of filter paper/polymer minus the initial weight of filter paper. Results were reported as percent polymer formed by weight of
- 15 polymer formed in mgs divided by the weight of the original styrene monomer used in mg multiplied by 100.

Results

- Uninhibited styrene monomer prepared by the above procedure stored at -25°F ($-$
- 20 13°C) was used to evaluate the additives of the instant invention, as described below. As noted, a 90 minute nitrogen reflux test method was used to generate the data. Table I summarizes the results from the initial testing.

TABLE I — Polymerization Inhibition Using Various Components

<u>Ex.</u>	<u>Additive</u>	<u>Concentration (ppm)</u>	<u>Percent Polymer</u>
1	none	—	36
2	4-OH TEMPO ¹	35	14
3	4-OH TEMPO	125	6.0
4	4-OH TEMPO	150	4.0
5	4-OH TEMPO	500	2.6
6	4-Tert-butyl-pyrocatechol	125	14
7	TETRALIN ²	125	18
8	Tert-butyl HQ ³	125	18
9	2,5-Di-tert-butyl HQ	125	16

¹ 2,2,6,6-Tetramethyl-4-hydroxypiperidine-1-oxyl

² 1,2,3,4-Tetrahydronaphthalene; this test was stopped after 60 minutes.

³ HQ = hydroquinone

TABLE II

Polymerization Inhibition Using Various Components

The data below summarizes the results of selected combinations of additives

5 described in the instant invention.

<u>Ex.</u>	<u>Additive</u>	<u>Concentration (ppm)</u>	<u>Percent Polymer</u>
19	4-OH TEMPO	35	
	Tert-butyl HQ	35	11
20	4-OH TEMPO	125	
	Tert-butyl HQ	125	5.3
21	4-OH TEMPO	125	
	4-Tert-butyl-catechol	125	6.0
22	4-OH TEMPO	180	
	Tert-butyl HQ	180	5.3

TABLE III

Polymerization Inhibition Using Various Components

The data below summarizes the results of selected combinations of additives

10 described in the instant invention formulated in n-octyl amine.

<u>Ex.</u>	<u>Additive</u>	<u>Concentration (ppm)</u>	<u>Percent Polymer</u>
23	4-OH TEMPO in n-octyl amine	125	5.0
24	4-OH TEMPO	125	
	Tert-butyl HQ in n-octyl amine	125	4.0
25	4-OH TEMPO	125	
	DHA ¹ , in n-octyl amine	180	4.3
26	4-OH TEMPO	125	
	2,5-di-tert-butyl HQ	125	0.42
	in n-octyl amine		

¹ 9,10-Dihydroanthracene

TABLE IV

Polymerization Inhibition Using Various Components

The data below summarizes the results of multiple combinations of additives of the invention formulated in n-octyl amine.

<u>Ex.</u>	<u>Additive</u>	<u>Concentration (ppm)</u>	<u>Percent Polymer</u>
27	4-OH TEMPO	125	0.93
	DHA	180	
	Tert-butyl HQ	180	
28	4-OH TEMPO	125	0.24
	TETRALIN	103	
	2,5-di-tert-butyl HQ	174	
29 ¹	4-OH TEMPO	125	0.12
	TETRALIN	103	
	2,5-di-tert-butyl HQ	174	
30	4-OXO TEMPO	125	0.77
	TETRALIN	103	
	2,5-di-tert-butyl HQ	174	

5

TABLE V — Example 31

The data below summarizes the amount of polymer formed during the duration of the test when using the combination of inhibitors: 125 ppm 4-OH TEMPO, 103 ppm TETRALIN, and 174 ppm 2,5-di-tert-butyl HQ all formulated in n-octylamine. The test apparatus is equipped with a septum and a 5 ml sample is extracted with a syringe at designated time intervals.

10

<u>Time</u>	<u>Percent Polymer</u>
0	0
15	0
30	0
45	0
60	0
75	0.05
90	0.15

TABLE VI

Example 32

The data below summarizes the amount of polymer formed during the duration of the test when using the combination of inhibitors: 52 ppm TETRALIN, 87 ppm 2,5-di-tert-butyl HQ, and 65 ppm 4-OH TEMPO formulated in n-octylamine. Samples were extracted as in Example 31.

15

¹ This Example was formulated in n-(2-aminoethyl)ethanol instead of n-octyl amine.

<u>Time</u>	<u>Percent Polymer</u>
0	0
15	0
30	0
45	0
60	0.1
75	0.62
90	1.2

TABLE VII

Example 33

Table VII shows that even when the di-hydroxyarene compound is not formulated in an organic amine the combinations of stable free radical, hydrogen transfer agent and di-hydroxyarene materials are still quite effective.

<u>Additive</u>	<u>Concentration (ppm)</u>	<u>Percent Polymer</u>
4-OH TEMPO	125	0.64
TETRALIN	103	
2,5-di-tert-butyl HQ	174	

TABLE VIII

Polymerization Inhibition Using Various Components

A 1000 ml of inhibited styrene monomer was distilled under vacuum and the freshly distilled styrene monomer material was immediately used to evaluate the instant invention. All the inhibitors are formulated with n-octyl amine.

<u>Ex.</u>	<u>Additive</u>	<u>Concentration (ppm)</u>	<u>Percent Polymer</u>
34	4-OH TEMPO	125	0.06
	TETRALIN	103	
	2,5-di-tert-butyl HQ	174	
35	4-OH TEMPO	125	0.06
	DHA	140	
	2,5-di-tert-butyl HQ	174	

The results indicate that the instant invention is even more effective on controlling polymer formation when using freshly distilled styrene.

15

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in providing a composition for inhibition of polymerization of vinyl aromatic compounds, such as styrene. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or scope of the invention as set forth in

20

the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific combinations of components, other than those specifically tried, in other proportions or ratios or added in different ways, falling within the claimed parameters, but not specifically identified or tried in a particular composition to improve the polymerization inhibition herein, are anticipated to be within the scope of this invention.

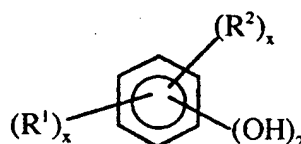
Claims

I Claim:

1. A composition for inhibiting polymerization of vinyl aromatic compounds comprising:

- a dihydroxyarene;
- a hydrogen transfer agent; and
- a stable nitroxide.

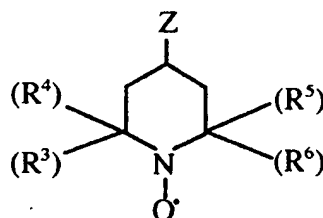
2. The composition of claim 1 where the dihydroxyarene has the formula:



where R^1 and R^2 are the same or different and are independently selected from the group consisting of hydrogen, straight, branched, and cyclic alkyl groups averaging from about 1 to about 6 carbon atoms, and where x averages from about 0 to about 9.

3. The composition of claim 1 where the hydrogen transfer agent is selected from the group consisting of naphthalene; anthracene; decalin; hydroquinoline; 1,2,3,4-tetrahydronaphthalene; 9,10-dihydroanthracene; fluorene; squalane; squalene; tetramethylhydroquinoline; and mixtures thereof.

4. The composition of claim 1 where the stable nitroxide has the formula:



where R^3 , R^4 , R^5 , and R^6 are the same or different and are independently selected from the group consisting of straight, branched, or cyclic alkyl groups of from 1 to about 9 carbon atoms; where Z is selected from the group consisting of hydrogen, oxygen, alkyl groups, alkoxy groups, hydroxyl, aryl groups, alkaryl groups, heterocyclic alkyl groups; and when Z contains carbon atoms, contains an average of from about 1 to 9 carbon atoms.

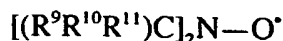
5. The composition of claim 1 further comprising an organic amine.

6. The composition of claim 5 where the organic amine has the formula:



where R^7 and R^8 are the same or different and are independently selected from the group consisting of hydrogen, straight, branched, and cyclic alkyl groups; alkoxy groups; hydroxyalkyl groups; and aminoalkyl groups; averaging of from about 1 to about 20 carbon atoms, where both R^7 and R^8 are not simultaneously hydrogen.

7. The composition of claim 1 where the stable nitroxide has the formula:



where R^9 , R^{10} , and R^{11} are independently selected from the group consisting of hydrogen straight, branched or cyclic alkyl, aryl, aralkyl, and alkaryl moieties;

where only one of R^9 , R^{10} , and R^{11} on each C can be hydrogen at a time;

where one or more of R^9 , R^{10} , and R^{11} on one C may be joined to a R^9 , R^{10} , and R^{11} on the other C to form a cyclic moiety selected from the group consisting of alkylene, and aralkylene moieties;

where any two of the R^9 , R^{10} , and R^{11} on any one C may be joined together to form a cycloalkyl;

where any of the above definitions of R^9 , R^{10} , and R^{11} may contain one or more heteroatoms selected from the group consisting of N, O and S; and

where the total number of carbon atoms in the hindered secondary hydroxylamine ranges from 6 to 70.

8. The composition of claim 1 where the components have the following proportions:

from about 1 to about 10,000 ppm of the dihydroxyarene;

from about 1 to about 10,000 ppm of the hydrogen transfer agent; and

from about 1 to about 10,000 ppm of the stable nitroxide,

based on the total amount of vinyl aromatic compound being treated.

9. A polymerization inhibited vinyl aromatic composition comprising:

a vinyl aromatic compound;

a dihydroxyarene;

a hydrogen transfer agent; and

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